HALL EFFECT IN SINGLE CRYSTALS OF GRAPHITE

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ABSTRACT. In view of the apparent differences in the results of Hall effect measurements on natural single crystals of graphite by different workers, it has been remeasured with some good crystals before and after the usual chemical purificatory treatments, adopting some special techniques. It has been shown that the Hall coefficient which is more or less independent of the magnetic field before the chemical treatments, shows irregular variations with magnetic field after these treatments and that such irregularities are beyond the limits of experimental errors. Posibility of these anomalies being associated with misalignments produced by chemical treatments has been indicated.

INTRODUCTION

Recent studies on the Hall effect in single crystals of graphite by Kinchin (1953), Berlincourt and Steele (1955) and Soule (1958) are very important since they could utilise their observations for deducing different electronic parameters of graphite and indicating (Soule 1958) the existence of new types of carriers in it. Kinchin observed that in cases of all the three specimens of single crystals sutdied by him, Hall coefficient at room temperatures remained always negative and independent of magnetic field down to about 600 oersteds. Soule on the other hand observed that in case of one of the two specimens studied by him Hall coefficient remained negative and practically independent of magnetic field down to about 350 oersteds then began to decrease very sharply and became positive at about 300 oersteds continuing to rise sharply with further decrease of field. But in the case of the other specimen the coefficient remained always negative and practically independent of field down to very low fields (of the order of 100 oersteds). It may be mentioned here that Soule had eleven different specimens at his disposal and he classified them according to their purities on the basis of magnetoresistance measurements but utilised for Hall effect measurements only two which are not the purer ones. The reason for this might be the fact that these two crystals behaved more or less similarly so far as magnetoresistance was concerned. Berlincourt and Steele who confined their measurements in the liquid helium range only and at magnetic fields from 6 to 25 kilo-oersteds obtained an oscillatory field variation of Hall coefficient like Soule under similar conditions of temperature and field but no such behaviour was observed by Kinchin at similar temperatures and upto the maximum field (10 kilo-oersteds*) used by him. Again, while Berlincourt and Steele (1955) obtained a negative coefficient for the average field variation of the Hall coefficient at temperatures of liquid helium, that obtained by Soule (1958) under similar conditions is positive and in the case of Kinchin (1953) the Hall coefficient which was always negative at these temperatures first increased with field and then decreased with the further increase of field. Besides these the sign of the Hall coefficient is found by Soule to change from negative to positive for both the specimens at low temperatures and moderate fields and for one specimen at room temperature and very low fields. These low field variations are very important in view of some theoretical predictions (Soule 1958) and need careful consideration. Further, the specimens of natural crystals of graphite used by these authors are subjected to the usual purificatory treatments to remove all foreign impurities which, as has been pointed out by Ray (1959), considerably enhances the mosaicity in structure already present to some extent in these natural crystals, and thereby affects the electrical and magnetic properties appreciably (Bhattacharya, 1959). It is therefore natural to expect that Hall effect in graphite is also affected by these structural defects.

In view of what has been stated above it appears therefore desirable to remeasure the Hall effect in graphite in order to obtain a set of values free from the said apparent contradictions so that the data can safely be utilised for discussion in the light of different theories proposed. The present paper gives an account of these measurements at room temperatures and at moderate fields. The observations at low temperatures which are in progress will be discussed in a subsequent paper.

EXPERIMENTAL

The measurements described in this paper were taken with some flakes of well developed single crystals of graphite obtained from Ceylon as also with some thin pieces of extruded samples of graphite having the direction of extrusion either parallel or perpendicular to the plane of the specimen. These specimens were cut into rectangular shapes before mounting them in the requisite holders for Hall effect measurements, taking care that no fresh structural defects are introduced by these cutting and manipulation processes.

It may be mentioned here that for avoiding shorting effect in Hall effect measurements it is essential that the specimens should be cut so as to have their length to breadth ratio not less than 4 (Fig. 1) (Isenberg *et al*, 1948). Since in the present investigation it was not convenient to cut the samples in this manner, we avoided this difficulty by designing our holder in such a way that the distance between the Hall probes can be altered easily. By this process the ratio of the

*From the curves published by Berlincourt and Steele and by Soule it is found that the oscillations are distinctly observable from fields of about 6.5 kilo-oersteds and at about 10 kilo-oersteds these are very prominent.

distance between the two current contacts at the two ends of the specimen to that between the Hall probes can easily be made 4. To be sure that by this process we are able to avoid the shorting effect we measured with such a holder the Hall coefficient of a piece of very pure bismuth for different distances between the Hall probes. The results are represented in Fig. 1 wherefrom it can be seen that the experimental points follow the same curve as that of Isenberg *et al* (1948) and that

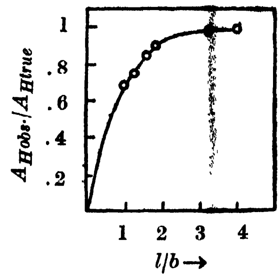

Fig. 1. Variation of Hall Coefficient with different length(l) to breadth (b) ratios. Full line curve is due to Isenberg and the points are from our observations. In our case the abscissa represents the ratio between l and distance between Hall probes δ.

the actual value of the Hall coefficient of bismuth is obtained when the ratio of the distance between current contacts to that between Hall probes is about 4. Under this arrangement the Hall coefficient A_H is given by

$$A_H = \frac{\Delta V.t}{H.i} \cdot \frac{b}{\delta} \quad 10^9 \text{ c.g.s. e.m.u.}$$

where ΔV is the Hall e.m.f. in volts, i the current through the sample in amperes, H the magnetic field in oersteds, and t, b, and δ are the thickness and the breadth of the sample, and the separation between the Hall probes, respectively, in centimeters.

Hall e.m.f.'s have been measured upto magnetic fields of about 7500 oersteds with a Pye precision vernier potentiometer reading down to 1 microvolt. The superimposed magnetoresistance, thermal and thermomagnetic effects have been eliminated in the usual way. The magnetic field was kept steady within 1 part in 1000 of any particular value by the manual operation of a fine motion accurate rheostat utilising a standard ammeter reading down to 10^{-2} amperes, the corresponding field being measured with the help of the magnecrystallic anisotropy of a paramagnetic crystal, so that an accuracy of 0.1 per cent (Dutta Ray, 1954) is obtained. The current through the sample was measured by observing the potential drop across a standard one ohm resistance connected in series with the crystal. The thicknesses of the specimens were measured with a standard micrometer and the lengths and breadths with a travelling microscope accurately to one hundredth of a millimeter. In consequence, for different samples, at a given field the values of the Hall coefficients are subjected to a maximum error of about 5 per cent and the corresponding limit of error in the study of magnetic field variation of the coefficient for a given sample is about 0.3 per cent.

Measurements with each sample of natural graphite crystal was undertaken before and after purification. The process of purification was the same as already described (Ray, 1959). The extruded samples however were not subjected to such purificatory treatments.

In addition to these observations an experiment was performed with a block of graphite made by stacking a number of graphite flakes one above the other and applying pressure on them. Current was passed perpendicular to the layers keeping the magnetic field transverse to the direction of current and Hall probes were placed midway between the two current contacts. The data obtained from observations with such a specimen will no doubt be far from reliable but the sign of Hall coefficient for current perpendicular to the basal plane will obviously be obtained with reasonable amount of definiteness. Experiment was also performed with a plate formed by pressing graphite powder.

RESULTS AND DISCUSSIONS

Fig. 2 represents the results of observations with single crystals of graphite before and after chemical purificatory treatments and Fig. 3 those with extruded samples, compressed plate of graphite powder and *c*-axis compact of natural flakes.

It is observed in cases of single crystals that before purification the Hall coefficient is on the average practically independent of magnetic field within the range of fields used, except in one or two cases at higher and lower extremities of the field. But after the usual purification has been done the Hall coefficient in every case vary with the magnetic field, the type of variation being quite different for different samples (see Fig. 2).

In order to explain these irregularities one may be tempted to associate such behaviours with the mosaicities in structure which, as is well known, (Ray, 1959) develop due to the chemical purification processes undertaken to remove foreign impurities from natural graphites. But before accepting such a view we took measurements with some polycrystalline samples of graphite. An extruded sample of graphite with currents parallel to the direction of extrusion, whose electrical conductivity for this direction has more or less the same value as that in the basal plane of a crystal, behaves similarly as an unpurified natural single crystal (Figs. 2 and 3). But with direction of current perpendicular to that of extrusion, in which case the number of misoriented crystalline blocks affecting the electrical resistivity will obviously be larger than in the earlier case, Hall coefficient is again seen to vary like those of purified samples of single crystals (Figs. 2 and 3). The compressed powdered sample which is evidently a highly defective crystal or a polycrystal also shows a variation of the Hall coefficient with field (Fig. 3). One may therefore suggest that these irregularities in the field variation of Hall coefficient are in some way connected with the crystalline defects. However, to establish a quantitative relation between the defects and the deviations from the normal field variation of Hall coefficient a detailed knowledge of the number of

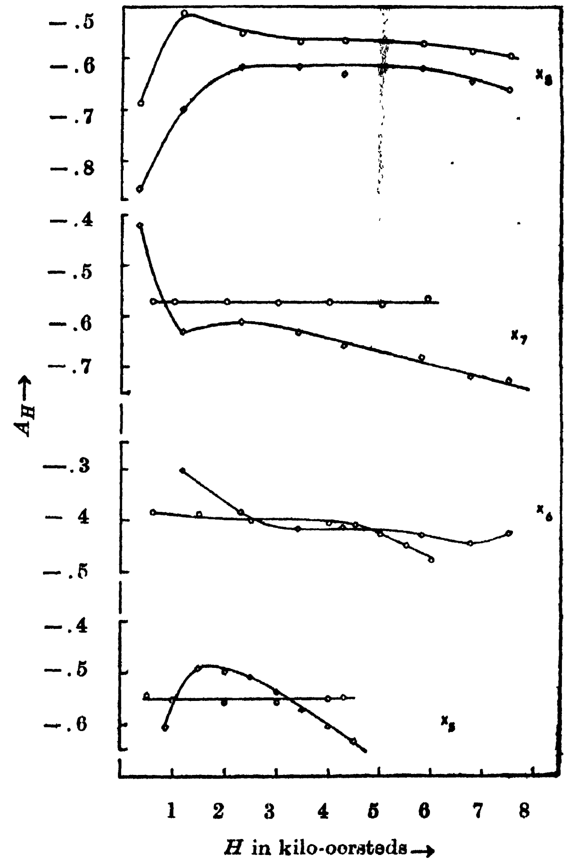

Fig. 2. Magnetic field variation of Hall coefficient of single crystals, X_5, X_6, X_7 and X_8 before and after chemical treatments.

O —Before chemical treatment

□ —After chemical treatment.

misoriented blocks with a particular value of misorientation and the manner in which these can affect the Hall effect is evidently necessary. This indeed is very difficult. However we are trying to do this by utilising the method we have developed for the purpose of finding the values of electrical conductivities and the magnetic susceptibilities of perfect crystals of graphite from a study of these properties of defective ones.

In this connection it would be interesting to reproduce here (Fig. 4) the room temperature observations of a some what similar nature by Soule (1958) who alone among the earlier workers made such observations. His specimens were, as already pointed out, defective. These irregularities as also their behaviour at low temperatures were explained by him as being due to the presence of some new types of carriers in graphite.

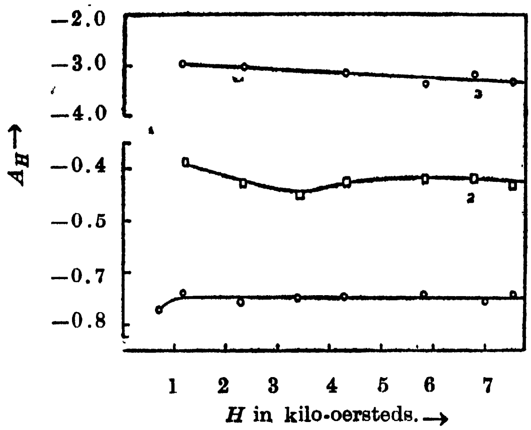

Fig. 3. Magnetic field variation of Hall coefficient of extruded and compressed samples.

Curve 1—extruded sample, direction of extrusion || to the plane.

„ 2— -do- ⊥ to the plane

„ 3—plate formed of compressed powder.

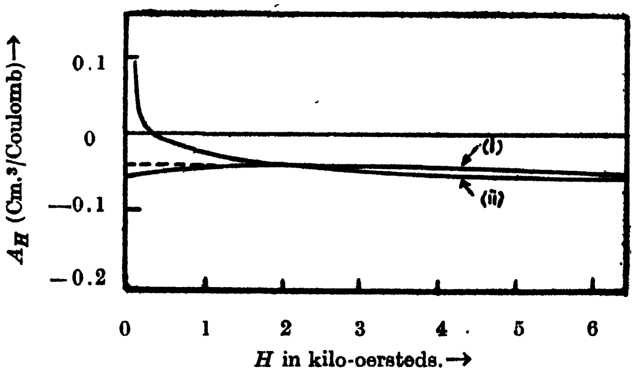

Fig. 4. Magnetic field variation of Hall coefficient of single crystals at room temperatures by Soule.

Curve 1—Specimen EP_{14}

„ 2—Specimen EP_7.

It therefore becomes apparent that these irregularities which we intend to associate with crystalline defects should also be studied at low temperatures before any definite conclusion is drawn. Work is in progress in this line and the results will be published soon.

It may be mentioned finally that the sign of the Hall coefficient has been found by us to be negative at all fields with all the different types of samples (single crystals, extruded samples, *c*-axis compact and powdered sample) studied.

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